$^{238}U/^{235}U$ RATIO IN CARBONATES AS A GLOBAL PALEOREDOX PROXY. C. Chen[1], F.L.H Tissot[1,2], N. Dauphas[1], A. Bekker[3], G.P. Halverson[4], J. Veizer[5], B.M. Go[1], M. Naziemiec[1], L. Shaw[1], G. Healy[1] [1]Origins Lab, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, Chicago, IL (chenxicindy@uchicago.edu), [2]Department of the Earth, Atmospheric and Planetary Sciences, MIT, Cambridge, [3]Department of Earth Sciences, University of California-Riverside, Riverside, CA, [4]Department of Earth and Planetary Sciences, McGill University, Montreal, Quebec, Canada, [5]Department of Earth and Environmental Sciences, University of Ottawa, Ottawa, Canada.

Introduction:

Uranium has two main oxidation states: 4+ and 6+. In the modern ocean, U is present in its most oxidized, highly soluble form, U^{6+} [1]. In the Archean, however, when the oxygen concentration in the atmosphere was low, U was likely present in its reduced 4+ state, which has low solubility. This contrast in solubility behavior depending on the redox conditions makes U a very useful proxy of the global oxygenation state of the Earth. Indeed, one of the most important indicators that the pO_2 was low in the Archean is the survival of detrital uraninite [2], which is unstable under the modern oxic conditions.

In addition to its oxidation state, the elemental abundances of U in marine sediments can bring further insights into the redox conditions in Earth's atmosphere and ocean [3, 4]. Additionally, several recent studies have shown the potential of U isotope ratios to provide further constraints on the redox conditions in the oceans through time [*e.g.*, 5-9]. So far, much focus has been devoted to analysis and interpretation of the shale record [5-6, 10-13]. A difficulty with black shale samples, however, is that they have highly fractionated U isotopic compositions relative to seawater, and it is unclear what controls this fractionation and whether it remained constant throughout Earth's history. An additional source of uncertainty is that shales can contain a significant portion of detrital U that needs to be corrected for [5, 13-14].

To circumvene these difficulties, we have decided to study U in the carbonate record. There are two main reason for this choice: (i) the U isotopic fractionation relative to seawater in modern carbonates is small [15], (ii) and the detrital component in these samples should be relatively minor and can easily by corrected for, if present. Furthermore, carbonate samples provide an extensive record of Earth's history.

Background:

Application of U isotopes as a paleoredox proxy relies on the fact that sediments precipitated under anoxic/euxinic conditions are enriched in ^{238}U relative to ^{235}U. Assuming that the oceanic U budget is at steady-state with regards to U isotopes (a valid assumption for the modern ocean, [9]), the seawater $\delta^{238}U$ value directly depends on the extent of global oceanic anoxia (*i.e.*, the fraction of U that is removed to anoxic sediments; Fig. 1). Therefore, estimates for the $\delta^{238}U$ value of seawater through time will provide constraints on the redox state of the global ocean. This is true provided that a rock record that faithfully tracks the U isotopic composition of the seawater can be identified.

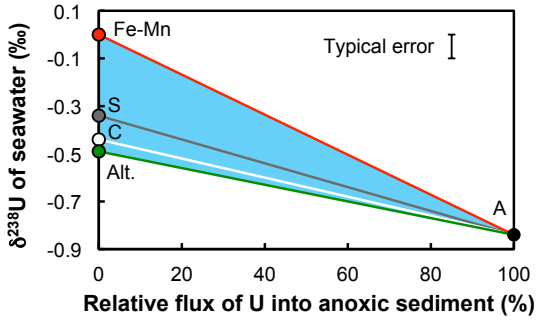

***Figure 1**: Expected $\delta^{238}U_{Seawater}$ value plotted as a function of the flux of U into anoxic sediments, relative to the total U flux out of the ocean. The sinks considered are: anoxic sediment (A), iron-manganese nodules and metalliferous sediments (Fe-Mn), suboxic sediments (S), carbonates (C), and altered oceanic crust (Alt.). Lines between the endmembers represent the evolution of the $\delta^{238}U_{Seawater}$ assuming that U is only incorporated in the two endmembers considered, and that the oceanic U budget is at steady-state.*

The fractionation factor associated with the carbonate sink is small [15], and varies much less than the one associated with the anoxic/euxinic sink. Thus, carbonates might potentially provide a more powerful and reliable record of the $\delta^{238}U$ of seawater than black shales. By measuring the U isotopic compositions of a large suite of marine carbonates, which span a broad time period, we aim to reconstruct the paleoredox conditions in the ocean through time. This first continuous record of ocean oxygenation can provide new insight into the redox conditions during the "boring billion" [16]: a billion year period of purported environmental and biospheric stasis that started with the disappearance of BIFs at ~1.8 Ga. The demise of BIFs is widely interpreted to reflect a major change in the global redox state of the ocean. The question remains, however,

as to whether the nature of this shift was towards more oxygenated, anoxic (ferruginous), or euxinic (anoxic + sulfidic) water column conditions.

Digestion protocol:

To avoid the impact of secondary processes and access the original $\delta^{238}U$ value recorded by the carbonate samples, a step-leaching protocol was developed. It is based on the idea that easily mobilized U, which is also more likely to be of secondary origin, can be selectively removed from the sample by partial digestion with a dilute acid. A progressive digestion experiment, with 10% increment digestion steps, was performed on modern carbonates (stony coral from Florida) with dilute acetic acid (20% by volume) to track the release pattern of U isotopes.

For the concentrations, the first few leachates are depleted in U, while those of the intermediate and late leachates vary around the bulk value. Moreover, the U fractions collected in each step have variable isotopic compositions that can be significantly different from the value of modern seawater [9]. In particular, early leachates show U isotopic composition heavier than seawater by up to 0.3 ‰, while the final leachates tend to have $\delta^{238}U$ lower than seawater by 0.1 to 0.2 ‰.

From the results of the sequential leaching experiment, a two step-leaching protocol was designed for application to carbonate samples. In the first leaching step only a small fraction of the carbonate is digested in order to remove easily mobilized U that could have an extraneous origin, then in a second step, the bulk of the carbonate is digested in order to access the original U isotopic composition of the carbonate sample. Care was taken to avoid dissolution of detrital fraction, which could contribute U from phases other than carbonates (*e.g.*, silicates), whose isotopic composition will likely be different from that of the carbonate.

Sample selection and processing:

More than 200 samples are currently being processed through the U isotopic analysis protocol (*i.e.*, step-leaching, column chemistry and high-precision measurement on MC-ICPMS) [see details in 9]. Each of the carbonate sample of this large collection was carefully selected so as to satisfy the following requirements: (1) the unit must be of marine origin (*i.e.*, sediment, deposited in the open ocean) in order to ensure that the signal recorded in the sample corresponds to the global ocean redox conditions, (2) the unit and sample must have experienced only limited secondary alteration in order to minimize elemental and/or isotopic resetting of the U systematics, (3) the entire sample set must span most of Earth's history, with a high temporal resolution.

Identification of the least-altered and best-preserved samples was based on a combination of petrological evidence and an array of geochemical tracers that reveal the extent of post-depositional resetting of geochemical signatures. For example, post-depositional fluid circulation enriches carbonates in Mn, and decreases their Sr/Ca ratios [17]. Thus, samples with the highest Sr/Ca ratio and lowest Mn concentration were selected in preference to other samples. Similarly, the isotopic compositions of oxygen and carbon were also considered, with preference given to samples characterized by higher $\delta^{18}O$ and $\delta^{13}C$ values, which are less likely to be affected by dissolution-reprecipitation during infiltration of diagenetic and basinal waters or hydrothermal fluids with mantle composition [18].

The results obtained from this study will be used to reconstruct the evolution of the marine redox conditions through time. Preliminary results will be presented at the conference on at least 50 samples that have already been measured.

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